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WIPO			PCT

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file CDK2138	FOR FURTHER A	CTION See Notification Preliminary	ution of Transmittal of International Examination Report (Form PCT/IPEA/416)		
nternational application f	No. International filing date 06.11.2003	(day/month/year)	Priority date (day/month/year) 08.11.2002		
ntemational Patent Class 023F11/00	l sification (IPC) or both national classification	and IPC			
Applicant RHODIA CONSUM	ER SPECIALTIES LIMITED et al.				
This internations     Authority and is	l preliminary examination report has be transmitted to the applicant according t	een prepared by this l o Article 36.	International Preliminary Examining		
2. This REPORT of	onsists of a total of 8 sheets, including	this cover sheet.			
This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).					
These annexes consist of a total of 4 sheets.					
3. This report conf	ains indications relating to the following	ı items:			
I ⊠ Bas	s of the opinion				
II 🔲 Prio			an and industrial applicability		
	-establishment of opinion with regard to	o novelty, inventive si	ep and industrial applicability		
V ⊠ Rea	and the second s				
	tain documents cited				
VII □ Cer	tain defects in the international applicat	tion			
VIII ⊠ Cer	tain observations on the international a	pplication			
Date of submission of t	he demand	Date of completion	n of this report		
25.05.2004		28.01.2005			
Name and mailing add	ress of the international	Authorized Officer			
preliminary examining ——————————————————————————————————	authority: n Patent Office - P.B. 5818 Patentlaan 2	Hondros Hells	M		
ML-2280 Tel. +31	HV Rijswijk - Pays Bas 70 340 - 2040 Tx: 31 651 epo nl	Handrea-Halle	er, IVI		

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/GB 03/04796

i.	Basis	of the	report
		<b>.</b>	

1. With regard to the **elements** of the international application (Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)):

	Desc	Description, Pages						
	1-9		as originally filed					
	Clain	ns, Numbers						
	1-16		received on 10.11.2004 with letter of 08.11.2004					
2.	With langu	regard to the languag	ge, all the elements marked above were available or furnished to this Authority in the rnational application was filed, unless otherwise indicated under this item.					
	Thes	e elements were avai	lable or furnished to this Authority in the following language: , which is:					
		the language of a trar	slation furnished for the purposes of the international search (under Rule 23.1(b)).					
	п .	the language of public	cation of the international application (under Rule 48.3(b)).					
		the language of a trar Rule 55.2 and/or 55.3	nslation furnished for the purposes of international preliminary examination (under ).					
3.	With inter	With regard to any <b>nucleotide and/or amino acid sequence</b> disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:						
		contained in the inter	national application in written form.					
		filed together with the	e international application in computer readable form.					
		furnished subsequen	tly to this Authority in written form.					
		furnished subsequen	tly to this Authority in computer readable form.					
	☐ The statement that the subsequently furnished written sequence listing does not go beyond the discloud in the international application as filed has been furnished.							
		The statement that the listing has been furn	he information recorded in computer readable form is identical to the written sequence					
4	. The	e amendments have r	esulted in the cancellation of:					
		the description,	pages:					
		the claims,	Nos.:					
		the drawings,	sheets:					
5	i. 🗆	been considered to	n established as if (some of) the amendments had not been made, since they have go beyond the disclosure as filed (Rule 70.2(c)).					
		(Any replacement s report.)	heet containing such amendments must be referred to under item 1 and annexed to this					
(	S. Ad	ditional observations,	if necessary:					

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/GB 03/04796

- V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- 1. Statement

Novelty (N)

Yes: Claims

2,5,13

No: Claims

1,3,4,6-12,14-16

Inventive step (IS)

Yes: Claims

13

No: Claims

1-12,14-16

Industrial applicability (IA)

Yes: Claims

1-16

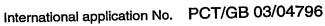
No: Claims

- 2. Citations and explanations
  - see separate sheet

## VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet



## **EXAMINATION REPORT - SEPARATE SHEET**

### Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

- The following documents are referred to in this communication: 1.1
  - D1: EP-A-0 780 406 (ALBRIGHT & WILSON UK LTD) 25 June 1997 (1997-06-25)
  - D2: EP-A-0 245 557 (TEXACO DEVELOPMENT CORP) 19 November 1987 (1987-11-19)
- 1.2 The following documents were not cited in the international search report. Copies of the documents are appended hereto.
  - D3: US-A-3 738 937 (TEXTILANA CORPORATION) 12 June 1973 (1973-06-12)
  - D4: EP-A-1 103 859 (KODAK POLYCHROME GRAPHICS COMPANY LTD) 30 Mai 2001 (2001-05-30)
  - D5: US-A-2001 018 965 (POLLOCK, VANDE SANDE & AMERNICK) 6 September 2001 (2001-09-06)
  - D6: US-B- 6 505 740 (HENKEL CORPORATION) 14 January 2003 (2003-01-14)
- 1.3 This International Preliminary Examination Report has been made as if the following clerical errors have been corrected:
  - Claims 4 and 9 as use not composition claims;
  - Claim 5 refers only to claim 3 and not to claim 4;
  - Claim 15 "copolymer" not "copolyme".

#### NOVELTY 2

The present application satisfies the criterion set forth in Article 33(2) PCT because 2.1 the subject-matter of claim 13 is new in respect to the prior art because none of the cited documents disclose a method in which the compound is applied to a metal prior to contact with water.

- 2.2 INDEPENDENT CLAIMS 1, 3, 6 and 12
- 2.2 The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1, 3, 6 and 12 is not new in the sense of Article 33(2) PCT.
- Document D1 (the references in parenthesis applying to this document) 2.2.1 discloses the use of an organophosphonate (i.e. BRIQUEST 543 = diethylenetriamine-pentakis (methylene-phosphonic acid)) or a copolymer of vinylidene-1, 1 di-phosphonic acid (VDPA) and vinylsulfonic acid (VSA) (i.e. 152DRW91 and 152DRW92) (cf. examples 9-11, 17, 18-21, claims 1-12) or the use of the maleic copolymer and acrylic polymer (cf. examples 23 and 24) or a composition of one of the above compounds and a dispersing agent, an additive, a corrosion inhibitor, etc. (cf. page 2, lines 50-54) to inhibit the corrosive action of the aqueous liquid on a aluminium surface (cf. page 3, lines 5-6, claim 18).

Because it is well-known that aluminium in the atmosphere and with water generates white rust consisting in aluminium oxide (see D5, col. 1, paragraph 4, lines 5-6 or D6, col. 10, lines 56-57) claims 1, 3 and 6 of the present application therefore lack novelty.

- Document D1 also discloses a method of inhibiting white rust corrosion with the 2.2.2 compounds or the composition described on the point 2.2.1 of the present communication (cf. example 23). Thus, the method of claim 12 of the present application lacks novelty.
- Document D2 (the references in parenthesis applying to this document) also 2.2.3 relates to the method and use of an organophosphonate (i.e BRIQUEST 543-33S= sodium diethylene-triamine-pentakis (methylene-phosphonate) (cf. example 2) or a composition of sodium diethylene-triamine-pentakis (methylene-phosphonate) and sodium polyacrylate (i.e dispersing agent) (cf. examples 8-9) to inhibit the corrosion attack of a aluminium surface (cf. page 2, lines 12-17). Thus, the subject-matter of claims 1, 3, 6 and 12 lack novelty.
- Document D4 (the references in parenthesis applying to this document) also 2.2.4 discloses the method and the use of an organophosphonate (i.e sodium

diethylene-triamine-pentakis (methylene-phosphonic acid)) or a copolymer of vinylidene-1, 1 di-phosphonic acid (VDPA) and vinylsulfonic acid (VSA) (cf. Table 2, claims 4-10) or composition of one of the above compounds and a dispersing agent, an additive, a corrosion inhibitor, a biocide, etc. (cf. claims 18, 23, 28 and 29) to inhibit the corrosive action of the aqueous liquid on a aluminium surface (cf. page 5, lines 23-25). Thus, the subject-matter of claims 1, 3, 6 and 12 lack novelty

## DEPENDENT CLAIMS 4, 7-11, 14-16

- 2.3 Document D4 (the references in parenthesis applying to this document) discloses the use of a copolymer of vinylidene diphosphonic acid and vinyl sulphonic acid in which the relative molar proportions may range from 1:1 to 1:1000, especially 1:10 to 1:100 (cf. page 3, line 58 to page 4, line 1) as well as the above copolymer and other water treatment agents including surfactants, chelating agents, corrosion inhibitors, threshold agents (e.g. sodium tripolyphosphate, acetodiphosphonic acid and its salts, ammonium trismethylene phosphonic acid and its salts; ethhylenediamine tetrakis (methylene phosphonic) acid and its salts, diethylenetriamine pentakis (methylene phosphonic) acid and its salts, biocides, polymeric dispersants (e.g. polyacrylic, polymaleic and polyvinylsulfonic acid and their salts) (cf. page 4, lines 37-56, claim 29). Claims 4 and 7-11 of the present application therefore lack novelty.
- 2.4 Document D4 (the references in parenthesis applying to this document) also discloses the use of a copolymer of vinylidene diphosphonic acid and vinyl sulphonic acid in an amount of 30 to 80 ppm (cf. page 5, lines 23-27, claim 24). Claims 14-16 of the present application therefore lack novelty.
- 2.5 Document D1 (the references in parenthesis applying to this document) discloses the use of a composition comprising a copolymer of vinylidene diphosphonic acid and vinyl sulphonic acid in a molar ratio in the range 1:99 to 99:1 (cf. page 2, lines 32-33, 47-49) and a dispersing agent, an additive, a corrosion inhibitor, etc. (cf. page 2, lines 50-54). Furthermore D1 discloses the use of the above copolymer in an amount of 50 ppm (cf. example 23). Claims 7 and 14-16 of the present application therefore lack novelty.
- 2.6 Document D2 (the references in parenthesis applying to this document) discloses the use of a composition comprising a phosphonated oligomer (i.e. sodium diethylenetriamine-pentakis (methylene-phosphonat)) and sodium polyacrylate (i.e dispersing

agent) (cf. examples 8-9) in which the polyacrylate is a low molecular polymer having a molecular weight in the range of about 500-6000 (e.g. 5100 in examples 8 and 9) (cf. page 5, lines 48-50). Claims 8 and 11 of the present application therefore lack novelty.

### 3 INVENTIVE STEP

- 3.1 The present application does not meet the criteria of Article 33(1) PCT, because the subject matter of claim 2 does not involve an inventive step in the sense of Article 33(3) PCT.
- 3.1.1 Document D1, which is considered to represent the most relevant state of the art to the subject matter of claim 1 (the references in parenthesis applying to this document), discloses the use of an organophosphonate (i.e <u>diethylene-triamine-pentakis</u> (methylene-phosphonic acid)) to inhibit corrosive action of the aqueous liquid on a aluminium surface (cf. page 3, lines 5-6, claim 18).
- 3.1.2 The subject-matter of dependent claim 2 differs from the disclosure of D1 in that the organophosphonate is a <u>bis(hexamethylene)</u>-triamine-pentakis (methylene-phosphonic acid).
- 3.1.3 Document D3 (the references in parenthesis applying to this document) discloses the use of <u>di-(hexamethylene)</u>-triamine-pentakis (methylene-phosphonic acid) as the preferred compound of the invention which have substantial corrosion protection properties (cf. col.5, lines 20-25, compound (2), Table IV, col. 9, lines 48-51).
- Therefore the features disclosed in D1 and D3 would be combined by the skilled person, without exercise of any inventive skills in order to solve the problem posed. The proposed solution in claim 2 thus cannot be considered inventive (Article 33(3) PCT).
- 3.2 The present application does not meet the criteria of Article 33(1) PCT, because the subject matter of claim 5 does not involve an inventive step in the sense of Article 33(3) PCT.

# INTERNATIONAL PRELIMINARY InteREXAMINATION REPORT - SEPARATE SHEET

- Document D4, which is considered to represent the most relevant state of the art to the subject matter of claim 5 (the references in parenthesis applying to this document), discloses the use of a copolymer of vinylidene diphosphonic acid and vinyl sulphonic acid in which the relative molar proportions may range from 1:1 to 1:1000, especially 1:10 to 1:100, e.g. 1:15 to 1:50 (cf. page 3, line 58 to page 4, line 1, example 4 (1:10)).
- 3.2.2 The subject-matter of dependent claim 5 differs from the disclosure of D4 in that the molar ratio is 1:20.
- 3.2.3 Since no indication can be found in the application as filed, which problem, compared with the state of the art disclosed in D4, has been solved by the feature disclosed in claim 5 of the present application, the subject-matter of claim 5 is not allowable for lack of inventive step.

### 4 INDUSTRIAL APPLICABILITY

4.1 The invention shall be considered as susceptible of industrial application because it can be used in the corrosion inhibiting industry.

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### **CLAIMS**

1. Use of an organophosphonate having the general formula (I):

5 wherein

 $Z = -CHR_1PO_3R_2$ 

R = H,  $CH_3$ ,  $C_2H_5$  or M

 $R^1 = H_1$ ,  $CH_3$ ,  $CR_3$ ,  $C_6H_5$ , or  $SO_3H_2$ 

M = alkali metal or ammonium ion

10 n = 0 to 10

m = 0 to 10

a = 0 to 10

 $\mathbf{b} = 0 \text{ to } 10$ 

c = 0 or 1

15 x = 0 to 10

y = 0 to 10

to inhibit white rust corrosion in water using systems.

Use as claimed in Claim 1, in which R and R<sup>1</sup> each = H, n = 6, m
 = 6, c = 1, y = 0 whereby the compound is bis(hexamethylene)triamine-pentakis (methylene phosphonic acid), as in formula (II):

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$$Z_2 N- (CH_2)_6 - N-(CH_2)_6 - NZ_2$$
 (II)

$$Z = CH_2 PO_3 H_2$$

- 3. Use of a random copolymer of vinylidene diphosphonic acid and vinyl sulphonic acid in a molar ratio of between 1:1 and 1:500 to inhibit white corrosion in water using systems.
- 4. A compound as claimed in Claim 3, in which the molar ratio is 1:100 molar.
- 5. Use as claimed in Claim 3 or Claim 4, in which the molar ratio is 1:20 molar.
  - 6. Use of a composition comprising a phosphonated oligomer of formula (I) as defined in Claim 1 or a random copolymer of vinylidene diphosphonic acid and vinyl sulphonic acid in a molar ratio of between 1:1 and 1:500, together with additives conventionally used in the water treatment industry to inhibit white rust corrosion in water using systems.
  - 7. Use as claimed in Claim 6 in which the additives are selected from the group consisting of phosphonocarboxylic acids or salts and dispersants.
  - 8. Use as claimed in Claim 7 in which the dispersant is a polyacrylate.
- 25 9. A composition as claimed in any one of Claims 6 to 8 in which the composition comprises a biocide.

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10. Use as claimed in any one of Claims 6 to 9 in which the phosphonocarboxylic acid or salt is a phosphonated oligomer of maleic acid, of general formula (III):

5 H[CHCO<sub>2</sub> MCHCO<sub>2</sub>M]<sub>n</sub> PO<sub>3</sub> M<sub>2</sub>

(III)

wherein M is a cation such that the oligomer is soluble in water, and n is greater than 1.

- 10 11. Use as claimed in any one of Claims 6 to 9, in which the polyacrylate compound is a low molecular weight polymer having a molecular weight between 2000 to 5000.
- 12. A method for inhibiting corrosion in, or in connection with, a water-using system, said method consisting of the application or addition to said system of an effective amount of a phosphonated oligomer of formula (I) as defined in Claim 1 or a random copolymer of vinylidene diphosphonic acid and vinyl sulphonic acid in a molar ratio of between 1:1 and 1:500 or of a composition comprising a phosphonated oligomer of formula (I) as defined in Claim 1 or a random copolymer of vinylidene diphosphonic acid and vinyl sulphonic acid in a molar ratio of between 1:1 and 1:500, together with additives conventionally used in the water treatment industry to inhibit white rust corrosion in water using systems...
- 25 13. A method as claimed in Claim 12 in which the method consists of the application to a metal prior to contact with water of an effective amount of the phosphonated oligomer or the random copolymer of vinylidene diphosphonic acid and vinyl sulphonic acid or of the composition.



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- 14. A method as claimed in Claim 12 or 13, in which the oligomer or copolymer is used in an effective amount of up to 1000 ppm.
- 15. A method as claimed in Claims 12 to Claim 14, in which the oligomer or copolyme` is used in an effective amount of up to 250 ppm.
  - 16. A method as claimed in any one of Claims 12 to 15 in which the oligomer or copolymer is used in an effective amount of up to 100 ppm.